ULTRAVIOLET ABSORPTION SPECTRA OF PHENYL ACETONITRILE, PHENYL ACETATE, PHENYL SALICYLATE AND MONOMERIC STYRENE IN THE LIQUID AND SOLID STATES*

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ABSTRACT. Absorption spectra of phenyl acetonitrile, phenyl acetate, phenyl salicylate and monomeric styrene in the liquid and solid states at low temperatures have been investigated and the results have been compared with those for vapours and for solutions of these substances. Absorption spectrum of phenyl salicylate in the vapour state has also been studied and the prominent bands have been assigned.

In the liquid state phenyl acetonitrile gives five broad bands with the 0,0 band at 37844 cm^{-1}, while in the vapour state the 0,0 band is at 38010 cm^{-1}. In the solid state at —180°C the 0,0 band shifts to 37917 cm^{-1} and the excited electronic state is found to be split up into two components.

Phenyl acetate in the liquid state yields four broad bands with the 0,0 band at 37554 cm^{-1}. The bands do not seem to undergo any change with changes of state except that the bands become a little sharper at the low temperature.

Phenyl salicylate in the liquid state gives a very broad band with the absorption edge on the longer wavelength side at 31306 cm^{-1} taken as the 0,0 band. The 0,0 band due to the vapour state has been found at 36342 cm ^{1}. Thus major change is found to occur on the liquefaction of vapour. In the solid state at —180°C the spectrum gives four narrower bands with the 0,0 band at 31046 cm^{-1}.

The liquid state of monomeric styrene yields five broad bands with the 0,0 band at 34228 cm^{-1} while that for the vapour state is at 34761 cm^{-1}. In the solid state at —180°C, the 0,0 band shifts to 34215 cm^{-1} and the excited electronic state is found to be split up into two components giving rise to thirteen bands. It has been suggested that two types of molecules formed by two types of associated groups of molecules in the crystal may give rise to the splitting of electronic energy level.

INTRODUCTION

In a previous investigation (Sen, 1955) it was observed in the case of *o*- and *p*- tolunitriles ($CN\ C_6H_4CH_3$) that $C \equiv N$ as a substituent in the aromatic ring

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has got an influence on the electronic energy levels of the molecules in the state of aggregation different from that observed in the case of molecules having halogen atom as a substituent (Swamy 1952, 1953). It was observed that major change in the absorption spectra occurs with the liquefaction of vapours of both the nitriles and the 0,0 band shifts towards longer wavelengths with the solidification of the liquids and lowering of temperature to $-180°C$, further shift towards longer wavelengths was observed in the case of the ortho compound, but no such shift takes place in the case of para compound. In tolunitrile the $C \equiv N$ group is attached to the benzene ring. The influence of the introduction of $C \equiv N$ group in CH_3 group of toluene on the ultraviolet absorption spectra of the compound in the state of aggregation is not known. Therefore, the ultraviolet absorption spectra of phenyl acetonitrile ($C_6H_5CH_2CN$) in the liquid and solid states have been studied in the present investigation. The results have been compared with those for vapour state reported by Imanishi and Kanda (1949) and with those for other substituted toluenes reported by Swamy (1952, 1953).

The ultraviolet absorption spectra of esters of benzoic acid in the liquid and solid states were studied by Deb (1951, 1953). It was observed by him that although in the case of halogen substituted benzenes the bands become sharp when the liquids are frozen and cooled to $-180°C$, in the case of alkyl benzoates the bands remain almost as broad as in the case of the liquid state when the liquids are frozen and cooled to $-180°C$. These benzoates may be regarded as substituted benzenes in which the substituent is attached to the benzene ring through a C-C bond. It was thought worthwhile to compare these results with those for esters of aliphatic acids containing CH_3 group and for esters containing two substituted benzene rings. Phenyl acetate and phenyl salicylate have been chosen for this purpose in the present investigation. The ultraviolet absorption spectra of phenyl acetate in the liquid and solid states have been investigated and compared with those for the vapour and the solution in ether reported by Kato and Someno (1938).

The absorption spectra of phenyl salicylate in the vapour state was not studied by any previous worker. So, the spectra of the compound in all the three states have been studied and the results have been discussed in the present paper.

The ultraviolet absorption spectra of monomeric styrene in the liquid and solid states were studied by Nikitana (1953) and he reported three bands in the liquid state which split up into twelve narrow bands in the solid state at $-195°C$, the continuous spectrum being resolved into seven wide bands. The original Russian journal being not available, it is not also known whether the results of absorption spectra of the liquid and solid states have been compared with those

for the vapour state in order to find out whether in the case of this substituted benzene containing a C = C group in the substituent, the influence of intermolecular field is the same as in other substituted benzenes in the solid state at low temperature. So the absorption spectra of monomeric styrene in the liquid and solid states have been reinvestigated and the results have been compared with those for the solution in cyclohexane reported by Robertson, Music and Matsen (1950) and that of vapour state reported by Morgan (1953).

EXPERIMENTAL

Chemically pure samples of phenyl acetonitrile and phenyl acetate s p-plied by Fisher Scientific CO., (U.S.A), phenyl salicylate supplied by E. Merck (Germany) and styrene monomer supplied by the Department of Physical Chemistry of this Association*, were distilled four times under reduced pressure before being used in the present investigation.

The experimental set up is the same as that employed in an earlier investigation by the author (Sen, 1955). Spectrograms were taken on HP 3 films with a Hilger El quartz spectrograph having a dispersion of 3 AU per mm in the region 2600°A. The absorption spectrum of phenyl salicylate in the vapour state was photographed using an absorption tube of length 50 cm and diameter 14 mm, quartz windows being cemented to the tube with Araldite. An exposure of 10 minutes was required to record the spectra for the liquid, while that for the spectra of the solid at −180°C was one hour. The spectrum of phenyl salicylate in the vapour state was recorded with an exposure of one and a half hours. In the case of liquid and solid states thin films of thickness less than .01 m.m. were used.

Iron arc was photographed on each spectrogram as comparison. Microphotometric records were obtained with a self-recording microphotometer supplied by Kipp & Zonen. The frequencies of the bands were measured from these records in which the record of two known iron lines were taken as reference lines. The microphotometric record of the iron lines was used as comparison.

RESULTS

The spectrogram of the vapour state of phenyl salicylate is reproduced in figure 1.

The microphotometric records of the spectrograms due to the substances in the liquid and solid states are given in figures 2, 3, 4 and 5. The frequencies of the bands are given in the Tables I, II, III, IV and V with approximate relative intensities indicated as strong, medium, weak etc.

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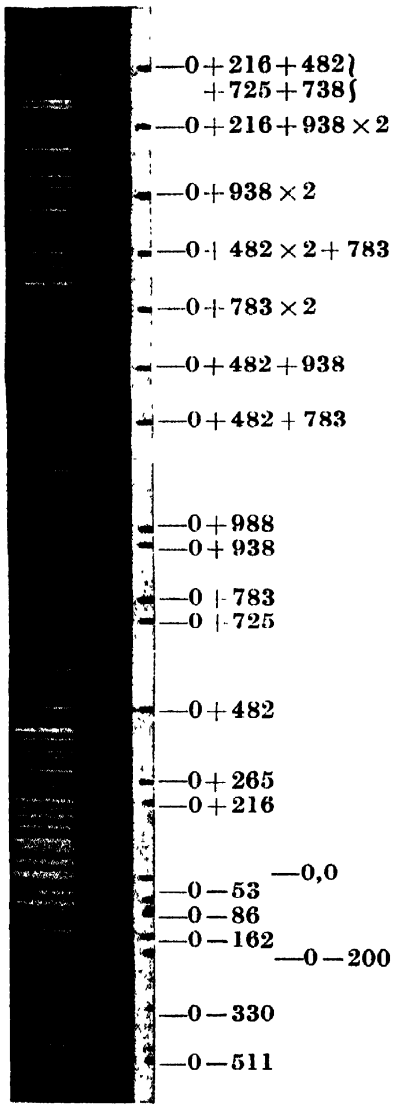

Fig. 1.
Ultraviolet absorption spectrum of phenyl salicylate vapour at 50°C.

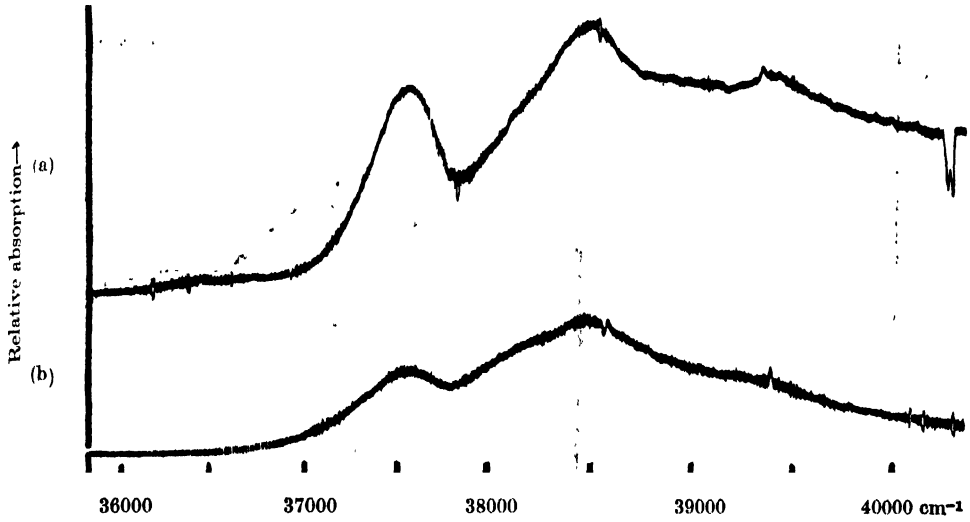

Fig. 2. Microphotometric records of the ultraviolet absorption spectra of phenyl acetate.
Curve (a)-Solid at —180°C. Curve (b)-Liquid at 30°C.

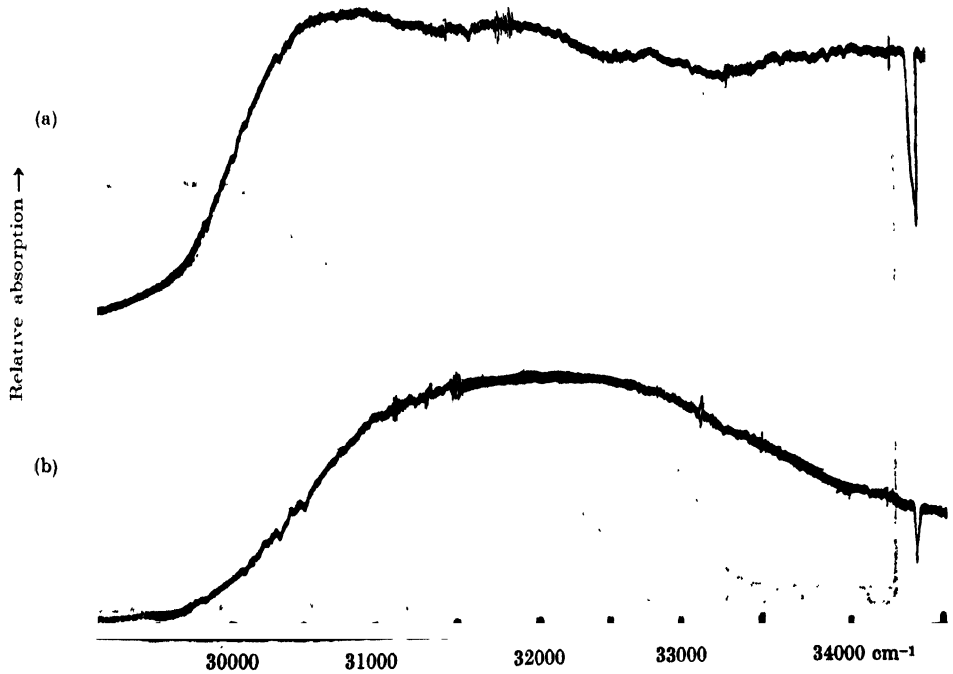

Fig. 3. Microphotometric records of the ultraviolet absorption spectra of phenyl salicylate.
Curve (a)-Solid at —180°C. Curve (b)-Liquid at 42°C.

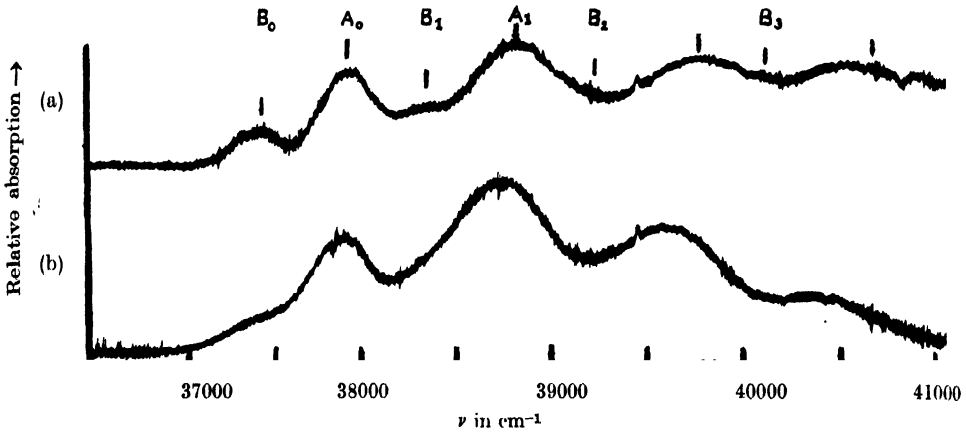

Fig. 4. Microphotometric records of the ultraviolet absorption spectra of phenyl acetonitrile.
Curve (a)-Solid at —180°C. Curve (b)-Liquid at 32°C.

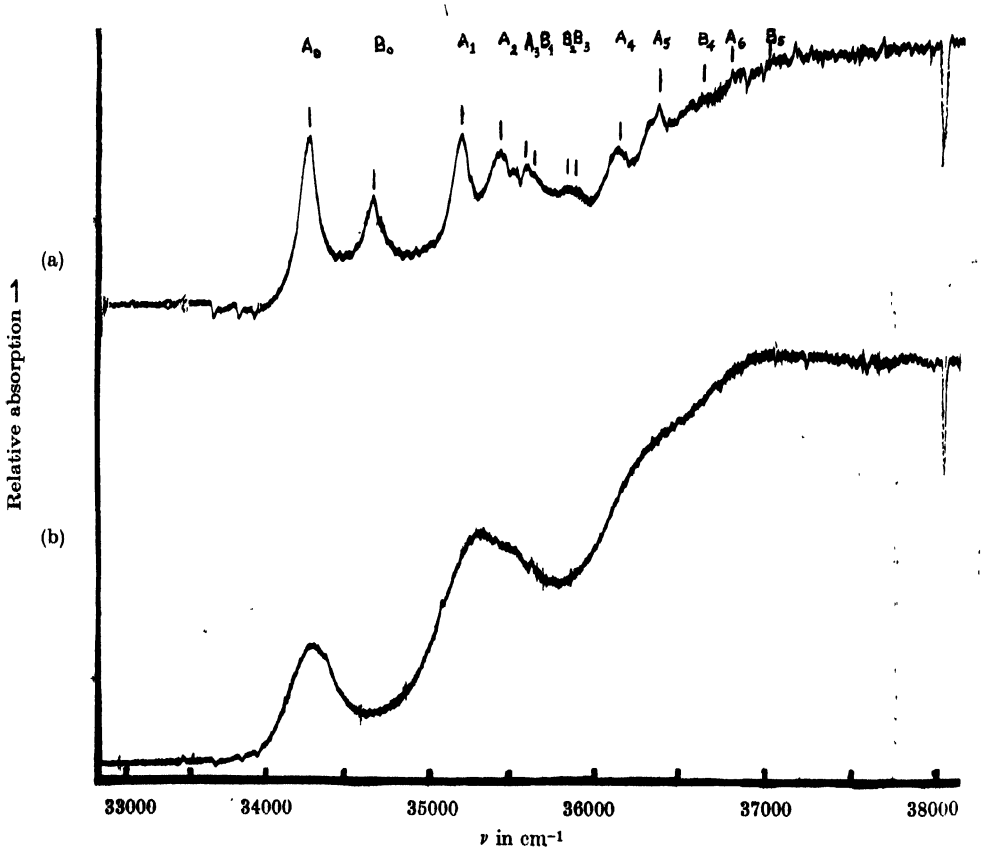

Fig. 5. Microphotometric records of the ultraviolet absorption spectra of monomeric styrene.
Curve (a)-Solid at —180°C. Curve (b)-Liquid at 30°C.

TABLE I

Absorption bands of phenyl acetonitrile in the liquid and solid states

Liquid at 32°C			Solid at −180°C		
Wave No cm^{-1}	Difference from 0,0 band	Assignment	Wave No in cm^{-1}	Designation	Assignment
37316 (vw)	−528	0−528			
			37404 (ms)	B_0	
37844 (s,b)		0,0			513
			37917 (s)	A_0	
38713 (vs,b)	869	0 + 869	38313 (w)	B_1	B_0 + 909
39590 (s,b)	1746	0+2×869	38826 (s,b)	A_1	A_0 + 909
40452 (ms, b)	2608	0+3×869	39219 (w)	B_2	B_0 + 909×2
			39727 (s, b)	A_2	A_0 + 909×2
			40138 (w)	B_3	B_0 + 909×3
			40634 (ms)	A_3	A_0 + 909×3

TABLE II

Absorption bands of phenyl acetate in the liquid and solid states

Liquid at 30°C			Solid at −180°C		
Wave No cm^{-1}	Difference from 0,0 band	Assignment	Wave No cm^{-1}	Difference from 0,0 band	Assignment
37554 (s, vb)		0,0	37556 (s, b)		0,0
38244 (w, vb)	690	0+690	38247 (w, b)	691	0+691
38494 (s, vb)	940	0+940	38496 (s, b)	940	0+940
38938 (w, vb)	1384	0+690×2	38939 (w, b)	1383	0+691×2
39435 (w, vb)	1881	0+940×2	39426 (w, b)	1870	0+940×2

TABLE III

Absorption bands of phenyl salicylate in the vapour state at 50°C

Wave No cm^{-1}	Difference from 0,0 band	Assignment	Wave No cm^{-1}	Difference from 0,0 band	Assignment
35831 (w)	−511	0−511	37125 (s)	783	0+783
36012 (w)	−330	0−330	37280 (s)	938	0+938
36142 (w)	−200	0−200	37330 (s)	968	0+988
36180 (w)	−162	0−162	37618 (ms)	1276	0+482+783
36256 (ms)	−86	0−86	37758 (ms)	1416	0+482+938
36289 (ms)	−53	0−53	37917 (ms)	1575	0+783×2
36342 (s)		0,0	38083 (w)	1741	0+482×2+785
36558 (ms)	216	0+216	38219 (w)	1877	0+938×2
36607 (ms)	265	0+265	38313 (w)	1971	0+988×2
36824 (s)	482	0+482	38433 (w)	2091	0+216+938×2
37067 (ms)	725	0+725	38556 (w)	2214	0+216+482+725 +783

TABLE IV

Absorption bands of phenyl salicylate in the liquid and solid states

Liquid at 42°C	Wave No cm^{-1}	Difference from 0,0 band	Assignment
Broad band extending from	31046 (s)		0,0
3199.5 Å (31245 cm^{-1}) to	31897 (ms)	851	0+851
3021 Å (33092 cm^{-1}). The aborption edge on	32755 (w)	1709	0+851×2
the longer wavelength side at 3193.3 Å (31306 cm^{-1}) taken as the 0,0 band. —Transmission in the region between 2981Å (33536 cm^{-1}) and 2666Å (37498 cm^{-1}) and continuous absorption thereafter.	33595 (w)	2549	0+851×3

TABLE V

Absorption bands of monomeric styrene in the liquid and solid states

Liquid at 30°C			Solid at −180°C		
Wave No cm^{-1}	Difference from 0,0 band	Assignment	Wave No cm^{-1}	Desig-nation	Assignment
34228 (s)	—	0,0	34215 (vs)	A_0	422
35224 (s)	996	0+996	34637 (s)	B_0	
35475 (ms)	1247	0+1247	35172 (s)	A_1	A_0+957
36223 (w)	1995	0+996×2	35434 (s)	A_2	A_0+1219
36726 (w)	2498	0+1247×2	35509 (ms)	A_3	A_0+1294
			35589 (ms)	B_1	B_0+957
			35854 (w)	B_2	B_0+1219
			35934 (w)	B_3	B_0+1294
			36123 (ms)	A_4	$A_0+957\times2$
			36399 (ms)	A_5	$A_0+957+1219$
			36549 (w)	B_4	$B_0+957\times2$
			36646 (w)	A_6	$A_0+1219\times2$
			36821 (w)	B_5	$B_0+957+1219$

DISCUSSION

Phenyl acetonitrile ($C_6H_5CH_2CN$)

The ultraviolet absorption spectrum of phenyl acetonitrile in the vapour state was studied by Imanishi and Kanda (1949) and the bands were classified according to the following series:

$$\nu = 38010+930u'+395v'-(765w''+145x'')$$

The intense band at 38938 cm^{-1} was not taken by them as the 0,0 band but it was assigned to 1,0 transition. In the present investigation, the liquid state yields five broad bands with the first band at 37316 cm^{-1}. This band is probably due to a $v\rightarrow0$ transition; if this weak band is taken as the 0,0 band, succeeding bands cannot be assigned properly. So the band at 37844 cm^{-1} is taken as the 0,0 band and a progression of excited state frequency 869 cm^{-1} is observed. The 0,0 band is found to be shifted by 166 cm^{-1} towards longer wavelengths from its position in the vapour state, probably due to formation of virtual bonds which lowers the excited electronic energy state. The excited state frequency 930 cm^{-1} observed in the case of the vapour corresponds to the frequency 869 cm^{-1}

in the excited state in the case of the liquid. In the case of the solid at low temperature eight bands are observed of which the first band on the longer wavelength side at 37404 cm^{-1} is weaker than the second one. It is found that all the bands cannot be assigned properly by taking this band as the 0,0 band, but if both the first and the second band are taken as the 0,0 band, all the bands are assigned and we get a progression of excited state frequency 909 cm^{-1}. Thus in this case the excited state energy level is split up into two components. The cynogen group is thus responsible for this splitting, but the 0,0 band does not shift very much with solidification of the liquid.

The weak band on the long wavelength side of the principal band marked. A_0 (figure 4) is at a distance of 513 cm^{-1}. The latter weak band cannot be due to $v \rightarrow 0$ transition as the large distance does not permit of molecules present in the excited state to have this mode of vibration. Also there is no strong band in the vapour state corresponding to this transition. The excited state frequency 909 cm^{-1} found in the case of the solid at $-180°C$, is larger than 869 cm^{-1} observed in the case of liquid. While the frequency 395 cm^{-1} observed in the case of the vapour is completely absent in the spectra due to the liquid and solid states, the aromatic ring vibration frequency seems to predominate in the excited state. Splitting of electronic energy level into three components was observed in the case of *o*-, *m*-chlorotoluenes, *o*-dichlorobenzene and *o*-bromotoluene by Swamy (1952, 1953). One of the two weak components was found to be on the longer wavelength side of the principal band in the case of *o*-chlorotoluene and *o*-dichlorobenzene just as the weak component in the present case, but in the case of *m*-chlorotoluene and *o*-bromotoluene both the weak components were on the longer wavelength side of the principal band.

Phenyl acetate ($CH_3.COO\ C_6H_5$).

The absorption spectrum of phenyl acetate in the vapour state was studied by Kato and Someno (1938). With the 0,0 band at 37500 cm^{-1}, the principal bands were assigned to progression of excited state vibration frequency 963 cm^{-1}. The bands were found to be broad and diffuse. In the present investigation the liquid state yields five broad bands represented by progression of excited state frequencies 690 cm^{-1}, 940 cm^{-1}. The 0,0 band of the liquid is at 37554 cm^{-1} So the 0,0 band does not shift very much with liquefaction of vapour. This indicates that the intermolecular field has very little influence on the electronic energy state in this case. The frequency 963 cm^{-1} found in the vapour state corresponds to excited state frequency 940 cm^{-1} in the liquid state. In the solid state at $-180°C$, the substance yields almost the same spectrum as in the liquid state except that the bands become a little sharper at low temperatures. The rotational freedom of the $0 - C = CH_3$ group about the C—0 bond may be responsible for the broadening of the bands in the vapour and liquid states.

In the case of solution of phenyl acetate in ether, three bands were reported by Kato and Someno (1938), the bands being at 37,700 cm^{-1}, 38,500 cm^{-1} and 39,300 cm^{-1} with the frequency difference of 800 cm^{-1} between successive bands. If this band at 37,700 cm^{-1} is taken as the 0,0 band, it is shifted by 146 cm^{-1} towards shorter wavelengths from its position for the liquid phase. This shift and the change in the excited-state vibration frequency show that the intermolecular field of the solvent exerts some influence on the electronic state of the molecule.

If these results are compared with those due to esters of benzoic acid (Deb, 1951, 1953), it is found that in the latter case the shift of the 0,0 band with change of state is much larger. Thus it appears that when the substituent in the benzene ring is connected through a C-C bond to the ring, the intermolecular field in the state of aggregation has a large influence on the electronic state but when it is connected through a C—O bond, the influence is small

Phenyl salicylate ($HOC_6H_4COOC_6H_5$)

The absorption spectrum of phenyl salicylate in the vapour state has not been reported by any previous worker. In the spectrum of the vapour obtained in the present investigation the intense band at 36342 cm^{-1} has been taken as the 0,0 band and assignments have been made only of the prominent bands. On the longer wavelength side of the 0,0 band there are some weak bands represented by transitions 0—162, 0—200, 0—330, 0—511 cm^{-1}. These vibrational frequencies correspond respectively to the Raman frequencies 163,191, 326, 504 cm^{-1} (Magat, 1936). The two bands on the longer wavelength side of the 0,0 band represented by transitions 0—53, 0—86 cm^{-1} are due to $v \rightarrow v$ transitions. The bands have been assigned to progression of excited state vibration frequencies 216, 265, 482, 725, 783, 938, 988 cm^{-1} and their combinations. The liquid state yields a very broad band extending from 31245 cm^{-1} to 33092 cm^{-1}. Further, the spectrum due to the liquid shows transmission in the region between 33536 cm^{-1} and 37498 cm^{-1} and thereafter continuous absorption. If the absorption edge on the longer wavelength side at 31306 cm^{-1} is taken as the 0,0 band, the spectrum shows that the 0,0 band shifts by 5036 cm^{-1} towards longer wavelengths from its position in the vapour state. Such a large shift towards longer wavelengths shows that owing to very strong association of molecules in the state of aggregation, there is a huge change in the excited electronic energy state. When the liquid is frozen and cooled to −180°C, the broad band exhibited by the liquid state splits up into four narrower bands and the 0,0 band shifts further by 260 cm^{-1} towards longer wavelengths from its position in the liquid state. As the excited state frequency 851 cm^{-1} is observed in the spectrum of the solid in place of 938 cm^{-1} for the vapour state, the intermolecular field has greater influence on this frequency in the solid state than in the liquid state.

Thus we find that in the case of the ester containing two substituted benzene rings the influence of intermolecular field on the positions and the widths of the bands and on the excited state vibration frequency is very large.

Monomeric styrene ($C_6H_5-CH = CH_2$)

The ultraviolet absorption spectrum of monomeric styrene in the vapour state was studied by Morgan (1953). The 0,0 band was observed to be at 34761 cm^{-1} and the bands were assigned to progression of excited state vibration frequencies 148, 478, 746, 948, 959, 1024, 1209, 1300, 1486 cm^{-1}. The liquid state, in the present investigation, yields five broad bands. The 0,0 band is at 34228 cm^{-1} and the successive bands are represented by progression of excited state frequencies 996 cm^{-1} and 1247 cm^{-1}. Evidently, the two bands at 959 cm^{-1} and 1024 cm^{-1} become broad and merge into one another to form the broad band at 996 cm^{-1} in the case of the liquid. Similarly the frequency 1247 cm^{-1} may be the mean of the two frequencies 1209 cm^{-1} and 1300 cm^{-1} observed in the case of the vapour. The 0,0 band of the liquid state is at a distance of 533 cm^{-1} towards longer wavelengths from its position in the vapour state

The bands in the spectrum of the solution of the substance in cyclohexane reported by Robertson and others (1950) are at 34354, 35387 and 36485 cm^{-1}. If the 0,0 band of the spectrum is assumed to be at 34354 cm^{-1}, it is found to be shifted towards shorter walvelengths by 126 cm^{-1} from its position in the spectrum of the pure liquid. The successive bands of the spectrum of the solution can be assigned as ν_0+1033, $\nu_0+2\times1033$ whereas frequencies observed in the pure liquid spectrum are 996 cm^{-1} and 1247 cm^{-1}. The shift of the bands and the change in excited state frequencies mentioned above furnish strong evidence for the existence of strong influence of the solvent molecules on the energy state of the molecule.

With the solidification and lowering of temperature to −180°C the 0,0 band of the pure substance shifts from 34228 cm^{-1} to 34215 cm^{-1} and it is spilt up into two components of unequal intensities. The weaker component marked B_0 is on the shorter wavelength side of the principal band marked A_0 (figure 5). Assignments have been made on the assumption that electronic energy level is split up into two components. Accordingly, as mentioned above, in place of five bands given by substance in the liquid state, thirteen bands are observed in the case of the solid state at −180°C. The splitting of the 0,0 band is probably due to the formation of virtual bonds between neighbouring molecules in the solid state. The very appearance of the two components suggests that two different types of molecules produce the two components and these two types of molecules are probably produced by formation of the two types of associated groups of molecules in the crystal. It cannot be indicated clearly how such different types of associated molecules are formed unless the crystal structure is

determined accurately. The excited state frequencies observed in the solid state are 957, 1219 and 1249 cm^{-1} and correspond to the frequencies 959, 1209 and 1300 cm^{-1} respectively found in the spectrum due to the vapour state. So, these frequencies do not undergo much change with change of state in this case.

Four low frequency Raman lines were reported by Roy (1954) in the solid state of the monomer at −180°C. The appearance of these low-frequency Raman lines may be explained by assuming them to be due to vibrations in associated groups of molecules mentioned above.

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